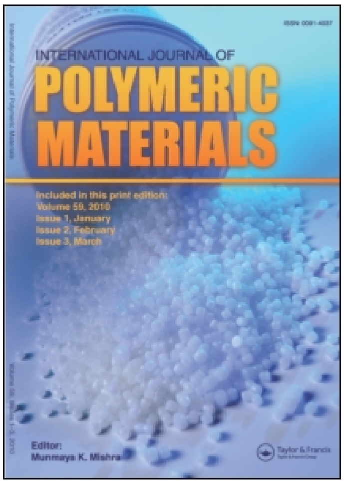

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Production, Physicochemical and Spectral-Luminescence Properties of Anthraquinone-Containing Polyamides

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Mono-, di-, and tri-staged methods of copolycondensation of the mixture of *m*-phenylenediamine and diaminoanthraquinones with isophthaloylchloride have been studied. A fraction of bound chromophore diamine and molecular mass of copolyamides formed have been shown to be defined by both basicity of initial diaminoanthraquinones and the copolycondensation method chosen. From the studies of physicomechanical, thermomechanical and spectral-luminescent characteristics of structural colored copolyamides the conclusion has been drawn that introduction of chromophore groups into polyamide chain in concentrations of 0.5–1.0% does not practically affect its submolecular structure.

Absorption and luminescence spectra have been investigated of solutions and films of polymethaphenyleneisophthalamide with fragments of diaminoanthraquinones in the chain, as well as those of aminobenzoylamine derivatives and dibenzoylamine derivatives simulating chromophore links of polymer chain. Character of alternation of chromophore groups in macromolecules has been established from comparative analysis of spectral and luminescence properties of the above structures.

KEY WORDS Aromatic polyamides, diaminoanthraquinones, spectral-luminescence.

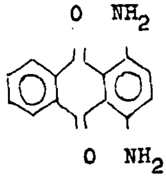
INTRODUCTION

Aromatic polyamides polymethaphenyleneisophthalamide (PMPIA) have found wide application recently due to their high physicomechanical and dielectric properties as well as satisfactory heat resistance.[1] To be used in certain branches of engineering these polyamides need to be brightly and uniformly colored, and the color must be resistant to various physicochemical effects. However traditional coloring (surface and in "mass") of the articles of these polymers does not often yield desirable results.[2,3] Therefore a possibility of introducing color molecules into polymer chain at the synthesis stage is now being intensively studied.[4] This method, called structural chemical modification of polymers, is quite broadly used to introduce anthraquinone and azobenzene fragments into aliphatic polyamide chain.[5–7] As for aromatic polyamides, attempts have been made to color them with the links of acridine[8] and rhodamine.[9]

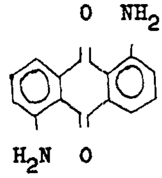
The cited works stated the possibility of obtaining modified polymers in such a way by the one-staged copolycondensation techniques. Their fiber and film-forming properties have been estimated. However due attention has not been paid to studying the structure of copolyamides and to clearing up the influence of chromophore fragments on physicochemical properties of polymers.

The problem on the nature of coloring centers and luminescence of the synthesized copolymers has not yet been properly studied. It is, however, one of the fundamental problems of traditional coloristics, concerned with establishing the form of the colorant (molecular or aggregate) responsible for the color of a particular article.

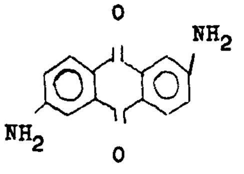
The present paper describes the synthesis of structural colored polymethaphenyleneisophthalamides as well as the structure, physicochemical and optical properties of the copolymers obtained. The following widespread disperse colorants were used as chromophore comonomers: 1,4-, 1,5-, 2.6-, diaminoanthraquinone and 4,8-diamino-1,5-dioxyanthraquinone. Their structures are shown in the figure below.



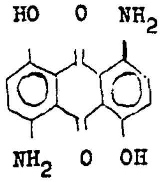
1,4-DAAQ



1,5-DAAQ

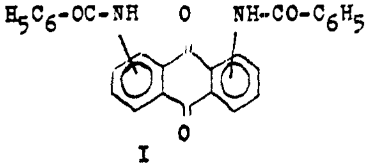


2,6-DAAQ

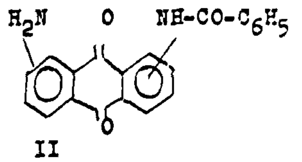


4,8-DADOAQ

Structure of molecular chains and nature of coloring centers of the copolyamides synthesized by copolycondensation of DAAQ and *m*-phenylenediamine with isophthaloylchloride have been established in comparative analysis of spectral-luminescence characteristics of solutions and films of polymers and low-molecular compounds simulating the chromophore fragments of polymer chains, such as aminobenzoylaminoanthraquinones (II) (ABAAQ) and dibenzoylaminoanthraquinones (I) (DBAAQ):



I



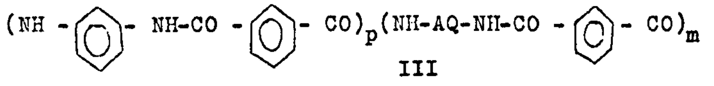
II

Synthesis of anthraquinone-containing polyamides was carried out in the following ways: mono-staged copolycondensation (polycondensation of stoichiometric quantity of isophthaloylchloride (IPC) and the mixture of *m*-phenylenediamine (MPDA) and 0.5–3.0 mass % diaminoanthraquinone); di-staged copolycondensation (oligoamide with the end amino-groups is obtained by reaction of 5% molar excess of MPDA and IPC in *N,N*-dimethylacetamide (DMAA), then the copolyamide is synthesized from corresponding diaminoanthraquinones and oligoamide with stoichiometric quantity of IPC); tri-staged copolycondensation (stoichiometric quantity of IPC is added to the mixture of oligoamide with the end amino-groups obtained by the di-staged copolycondensation technique and oligoamide obtained by polycondensation of 5% molar excess of diaminoanthraquinone with IPC).

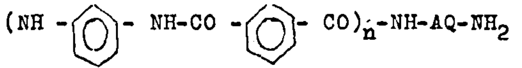
Polycondensation is conducted in DMAA medium, cooled to 0–5°C and the brightly colored solution obtained is treated with the mixture of DMAA-diethylamine to neutralize hydrogen chloride. Then the polymer solution is filtrated and formed on the laboratory spinning machine through a jet of 0.08 mm diameter into a setting bath with the water-DMAA mixture. The newly-formed fiber is subjected to drawing, washing of the solvent, drying, and thermal treatment according to techniques previously described.[10]

RESULTS

Table I gives the composition and properties of the synthesized polyamides of intensive coloring, the character of which depends on the nature of diaminoanthraquinone used. The evidence on insertion of colorants into the polyamide chain consists in the hypsochromic shift of the long-wave absorption band of the solutions of structural colored polyamides as compared to the same band of the initial diaminoanthraquinones and also in extraction of low-molecular colored products. This is particularly obvious in the case of polyamides with fragments of 1,4-DAAQ in the chain. The hypsochromic shift of the long-wave band testifies to the formation of the amido bond as a result of acylating one or two NH_2-groups in the substituted anthraquinones.[11] Therefore, depending on the nature of diaminoanthraquinone, copolyamides with structure III or IV were obtained as a result of copolycondensation:



III



IV

where AQ is the residue of 1,4-, 1,5-, 2,6-DAAQ or 4,8-DADOAQ.

TABLE I

Comparative physicochemical properties of anthraquinone containing polyamides and fibers on their basis

Chromophore comonomer	Synthesis method	Initial ratio MPDA:DAAQ[a]	[η]/g	Glass transition t, T_g °C	Strength, SH/tex	Elongation, %	Light resistance, %[c]	Coloring	
								Structural modified	Surface colored
1,5-DAAQ	I	99.0:1.0	1.69	—	—	—	—	Orange-red	Dark red
	II	98.97:1.03	2.24	278	44.9	22.2	90/82		
	III	99.02:0.98	2.10	278	42.1	27.4	85/69		
2,6-DAAQ	I	99.5:0.5	2.23	—	—	—	—	Yellow	Orange-yellow
	II	99.44:0.56	2.7	280	47.1	19.9	83/68		
	III	99.5:0.5	2.4	280	45.1	26.6	83/65		
1,4-DAAQ	I	99.5:0.5	1.95	—	—	—	—	Claret	Violet
	II	99.47:0.53	2.18	275	40	18	83/64		
4,8-DADOAQ	I	99.5:0.5	2.10	—	—	—	—	Blue-violet	Bright blue
	II	99.5:0.5	2.45	275	4.05	18	93		
PMPIA		—	2.30	278	42	19	83/65	White	White

[a] The ratios presented are optimum.

[b] Found from thermomechanical curves.

[c] Ratio of fibers strength after irradiation for 860 e s h (numerator) and 2630 e s h (denominator) to the initial strength.

Elsewhere[12] we showed that diaminoanthraquinones were characterized by somewhat lower values of ionization constants, pK_1 and pK_2, than MPDA. The values of pK_1 and pK_2 as well as those of acylation reaction rate constants can serve as criteria of diamines' reactivity in copolycondensation process. So it was to be expected that the colorants under study would not be present in the polymer chain in full. Some of them either do not participate in the reaction or only one aminogroup is subjected to acylation. As a result equimolality of diamine-dichloroanhydride components ratio is unbalanced and molecular mass of polymer drops.

Let us see to what extent the nature of chromophore diamines affects molecular mass of synthesizing copolyamides and actual content of fragments in their chain. Figure 1 shows the relationship between the amount of diaminoanthraquinone in the initial reactive mixture and the values of specific viscosity (η_{sp}) of copolyamides formed in the mono-staged synthesis in which the dosing rate of IPQ can be neglected. Copolycondensation of diaminoanthraquinones and MPDA results in formation of copolymers with somewhat lowered values of η_{sp} as compared with those of homopolymer (with the exception of 2,6-DAAQ). As DAAQ content in the mixture increases, the molecular mass of copolyamides decreases monotonically.

Table II gives the values of chromophores fragments bound to the polymer chain for various anthraquinone-containing polyamides (S). These were estimated by the change in optical density of long-wave absorption band of polymer solutions before and after purification from low-molecular colored products. The table also gives

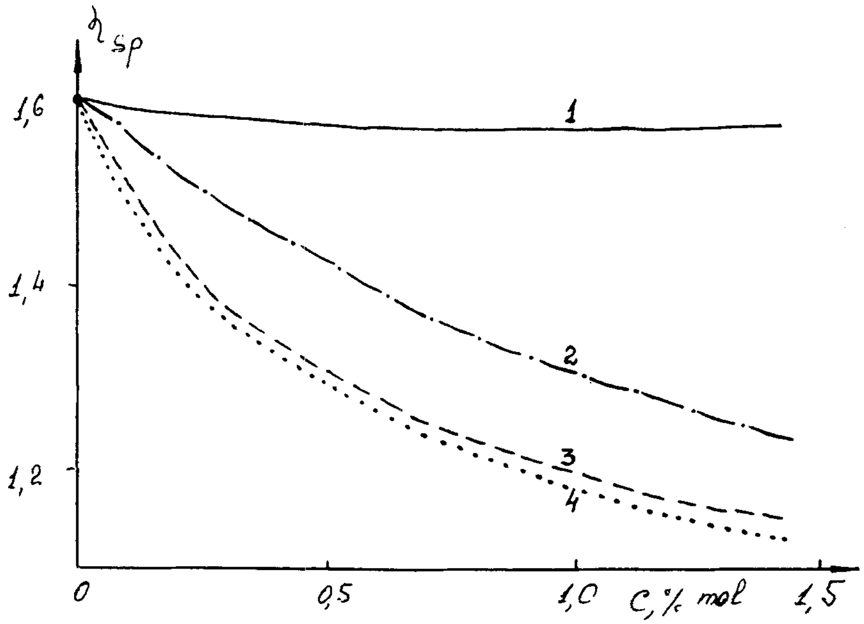


FIGURE 1 Dependence of specific viscosity of copolyamide solutions obtained in mono-staged copolycondensation upon diamine content in initial mixture: 2,6-DAAQ (1), 4,8-DADOAQ (2), 1,5-DAAQ (3) and 1,4-DAAQ (4).

TABLE II

Dependence between reactivities of amino-groups of anthraquinone derivatives and certain parameters of copolyamides on their basis (MPDA:DAAQ = 99.5:0.5 mole)

Initial diamine	Reactivity					Mono-staged method	
	pK_1	K_1	pK_2	K_2	pK_{av}[a]	S	η_{sp}
1,4-DAAQ	−0.07	0.0028	−3.4	0.0007	−1.73	0.73	1.28
1,5-DAAQ	−0.95	0.013	−2.29	0.0009	−1.62	0.62	1.31
4,8-DADOAQ	0.99	0.044	−2.22	0.0012	0.61	—	1.47
2,6-DAAQ	0.73	0.034	−1.00	0.0088	−0.14	0.97	1.57
MPDA	4.98		2.24		3.61		1.60

[a] $pK_{av} = \frac{pK_1 + pK_2}{2}$.

the parameters characterizing reactivity of diaminoanthraquinones[12] and the values of η_{sp} of anthraquinone-containing copolyamides. There is a direct proportion between the values of η_{sp} and reactivity of the first amino-group (pK_1 or k_1). Similar dependence was observed between the values of η_{sp} of copolyamides and pK_{av} that characterizes the mean reactivity of chromophore diamines.

The values of pK_2 and k_2 are likely to reflect the chain prolongation ability of chromophore oligomer with the end NH_2-groups belonging to anthraquinone fragments. To support this supposition is the comparison of spectral-luminescence data extracted from polymer low-molecular colored products (l.c.p.), structural colored polyamides and corresponding aminobenzoylamino- and dibenzoylaminoanthraquinones. For example, in the case of 1,4-DAAQ, with low values of pK_2 and k_2 and the biggest difference in the first and second-group reactivities ($k_1/k_2 = 39$), absorption and luminescence spectra of l.c.p. and structural colored copolyamide on the basis of this diamine are similar to those of 1-amino-4-benzoylaminoanthraquinone. The similarity of this kind indicates that one amino-group of 1,4-DAAQ is subjected to acylation and the chromophore fragment is localized along the ends of polymer chain.

At the same time oligomers with the end aminoanthraquinone fragments were not observed in l.c.p. for copolyamides based on 1,5-DAAQ ($k_1/k_2 = 14$). These products mainly consist of unreacted 1,5-DAAQ.

The features of mono-staged copolycondensation noted above are characteristic of the two-staged synthesis as well (Table II). The values of S and η_{sp} are somewhat higher in the case of distaged copolycondensation than those for the mono-staged case. This is obviously due to a lower dosing rate of IPC in the first case. At a low dosing rate of IPC a portion of chloroanhydride groups might not participate in the acylation process but side react with DMAA.

Of particular interest is the effect of chromophore fragments introduced into the polymer chain by various techniques of supermolecular structure of polyamides and physicochemical properties of the fibers on their basis. From Table I it follows that the highest-molecular polymers (maximum values) were synthesized by the di-staged copolycondensation method. For those structural colored polyamides (with the exception of polymers based on 1,4-DAAQ) the values of [α] are close to those of [α] for non-modified PMPIA.

The polymers obtained by different copolycondensation methods yield somewhat to PMPIA in the values of [α]. But regardless of the method of synthesis they all are quite high-molecular with good fiber-forming properties. The fibers on their basis are close in their physicochemical, thermochemical (glass transition temperature, T_g), and light resistance properties to the PMPIA fibers. Polyamide with 1,5-DAAQ and 4,8-DADOAQ fragments demonstrates somewhat increased stability to prolonged UV-irradiation effect (Table I).

X-ray differential, thermodifferential, and thermomechanical methods applied for studying copolyamides revealed no basic differences in supermolecular structure of modified and initial polymers.

Before studying spectral-luminescence properties of anthraquinone-containing polyamides, we shall analyze analogous properties of non-modified PMPIA. Absorption spectra of thin films and solutions of this polyamide are identical and represent an intensive band with λ_{max} at 310 nm and absorption edge spreading up to 390 nm. There is a band with λ_{max} = 440 nm in the fluorescence spectrum caused by defect links.[13]

Modification of PMPIA with diaminoanthraquinone fragments greatly affects its spectral properties. A long-wave band emerges in the absorption spectra of copolyamides, its maximum being dependent on the nature of initial colorant and on the form of the sample (film or solution). The results are presented in Table III and in Figures 2–5. Table IV lists the maxima of absorption and fluorescence bands of molecular and aggregate forms of model compounds (ABAAQ and DBAAQ).

Let us analyze spectral-luminescence properties of one of copolyamides obtained on the basis of 1,4-DAAQ CP(1,4-DAAQ) (Figure 2). In the upper part of Figure 2 there are spectra of solutions of CP(1,4-DAAQ) (3,3′)- and molecular form, 1-A-4-BAAQ(4,4′). A long-wave absorption and fluorescence band of solution CP(1,4-DAAQ) is seen to be similar to the corresponding bands of solution of 1-A-4-

TABLE III

Maxima positions in long-wave absorption and fluorescence bands of solutions (1) and films (2) of structural colored polyamides

Type of polyamide	Sample	Absorption λ_{max}, nm	Fluorescence λ_{max}, nm
CP(1,4-DAAQ)	1	510, 536, 576[a]	580, 612
	2	578,[a] 536	625
CP(1,5-DAAQ)	1	408,[a] 496	608
	2	408,[a] 496	608
CP(2,6-DAAQ)	1	430–580[b]	508, 580[b]
	2	450–560[b]	582[a]
CP(4,8-DADOAQ)	1	580, 628	642
		536, 586,[a] 630	Is absent

[a] Shoulder on spectral curve.

[b] Low-intensity band as a "tail."

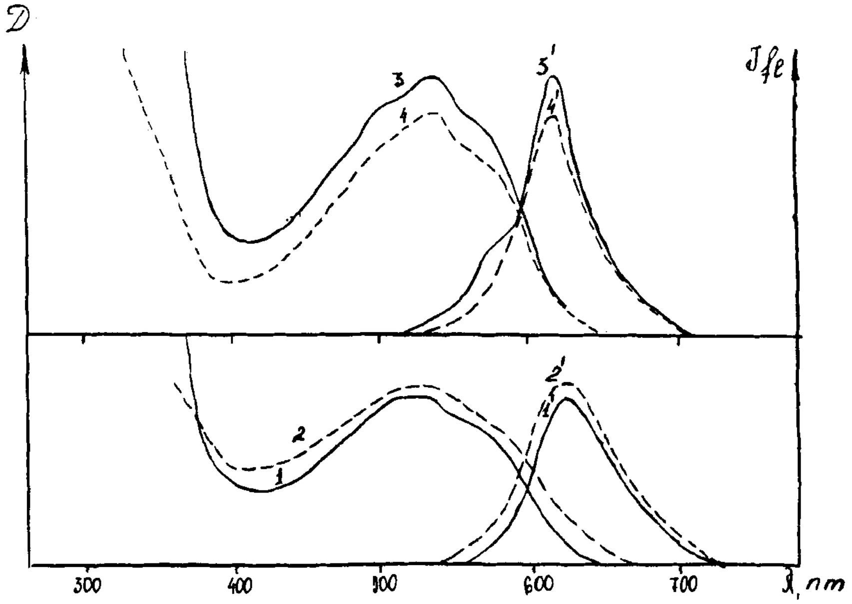


FIGURE 2 Absorption (1–4) and fluorescence (1'–4') spectra of solution (3,3') and film (1,1') of copolyamide CP(1,5-DAAQ), solutions of model compound of 1,5-DBAAQ in molecular (4,4') and aggregate (2,2') forms.

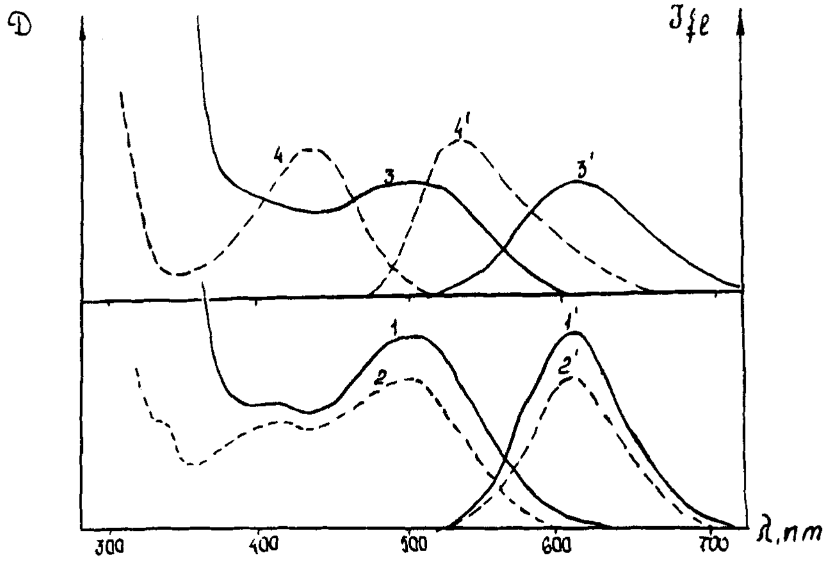


FIGURE 3 Absorption (1–4) and fluorescence (1'–4') spectra of solution (3,3') and film of copolyamide (1,4-DAAQ) (1,1), solutions of model compound of 1-A-4-BAAQ in molecular (4,4') and aggregate (2,2') forms.

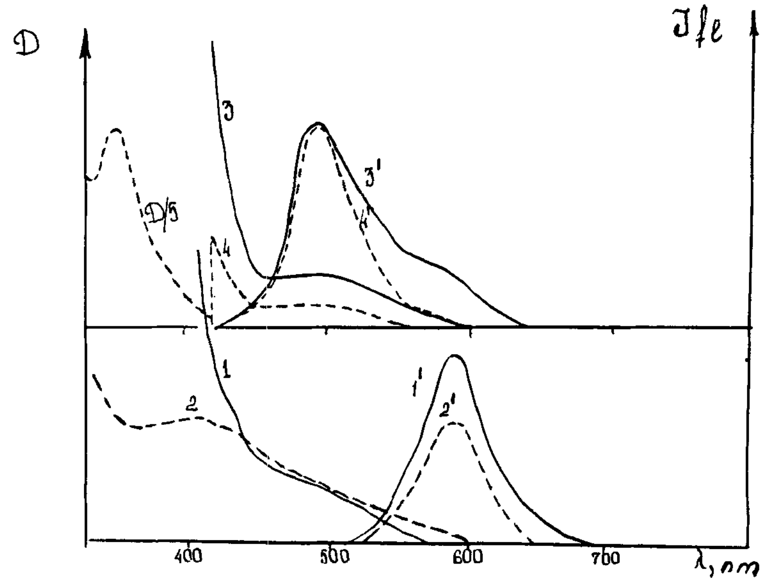


FIGURE 4 Absorption (1–4) and fluorescence (1'–4') spectra of solution (3,3') and film (1,1') of copolyamide CP(2,6-DAAQ), solutions of model compound of 2,6-DBAAQ in molecular (4,4') and aggregate (2,2') forms.

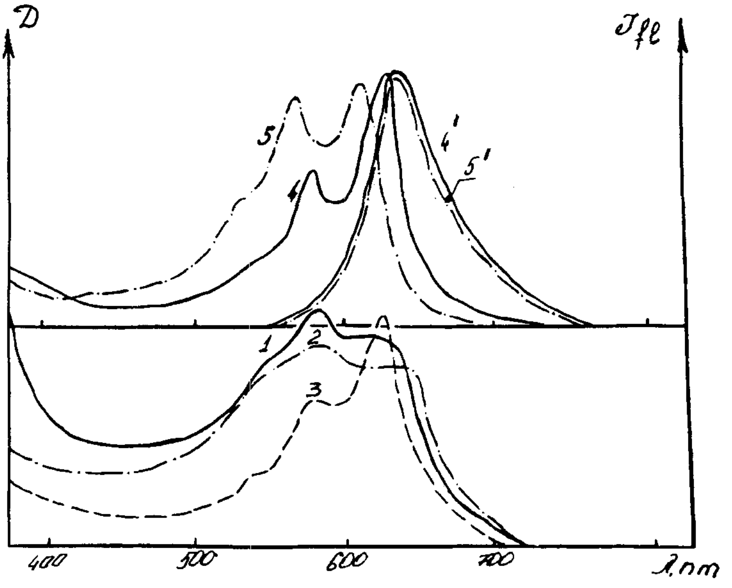


FIGURE 5 Absorption (1–5) and fluorescence (4',5') spectra of solution (4,4') and film (1) of copolyamide CP(4,8-DADOAQ), solutions of model compound of 4-A-8-BADOAQ in molecular (5,5') and aggregate (2) forms, and also solution of model compound of 4,8-DBADOAQ in aggregate form (3).

TABLE IV

Maxima positions in long-wave absorption and fluorescence bands of model compounds

Compound	Solvent	Absorption λ_{max}, nm	Fluorescence λ_{max}, nm
1,4-DBAAQ	DMAA	488	588
	Water	500, 515,[a] 575[a]	605
I-A-4-BAAQ	DMAA	510, 538, 576[a]	612
	Water	536, 578	625
1,5-DBAAQ	DMAA	436	586
	Water	408,[a] 496	608
1-A-5-BAAQ	DMAA	484	570
	Water	496	600
4,8-DBADOAQ	DMAA	545, 572[a]	613, 662[a]
	Water	590, 636	Is absent
2,6-DBAAQ	DMAA	356, 430–520[a]	508
	Water	408, 465[a]	582
2-A-6-BAAQ	DMAA	380, 460	565
	Water	420–520[a]	595

[a] Shoulder on spectral curve.

BAAQ. This similarity makes one suppose that chromophore fragment is localized along the ends of the polymer chain. In addition the chromophore fragment partially inserts into the main chain, as indicated by the bend in fluorescence curve of CP(1,4-DAAQ) solution at 580 nm similar to that in the emission band of 1,4-DBAAQ molecular form (Table IV). In the lower section of Figure 2 are the absorption and fluorescence spectra of CP(1,4-DAAQ) film and 1-A-4-BAAQ aggregate form. The similarity between these spectra is obvious. Luminescence of this film is represented by one luminescence center, i.e. fluorescence similar to the 1-A-4-BAAQ aggregate form. An analogous result was obtained for this copolyamide.

So the spectral data obtained testify to the fact that the color and luminescence of CP(1,4-DAAQ) is mainly determined by one center, i.e. interchain associates of chromophore links localized along the ends of polymer chain. Association of these links is connected with both their large (from the point of view of coloristics) polymer content (10^{-2}–10^{-3} mole/kg) and with the fact that macromolecules in amorphous films and concentrated solutions are rolled into statistical coils, inside which the mean concentration of links is high. That is why the probability of interaction between the chromophore links is large.[14] Heavy dilution of polymer solutions (up to 0.01 mass %) leads to the presence of isolated molecules in rolled and coiled conformations. This is reflected by the differences in the absorption and fluorescence spectra of the films and solutions of CP(1,4-DAAQ). To reduce intermolecular interaction between macromolecules LiCl was used.[1]

A somewhat different picture is observed with copolyamides containing the links of 1,5-DAAQ-CP(1,5-DAAQ) (Figure 3). Similarity of absorption and fluorescence spectra of the film and solution and also aggregate form of 1,5-DBAAQ is typical for this polymer, as well as the sharp differences of spectral characteristics of molecular form of this compound and 1-A-5-BAAQ (Figure 3, Tables III, IV). The spectral changes reported testify to the intramolecular association of chromophore fragments, or strictly speaking to the formation of irregular block-copolyamides in the process of synthesis. Further confirmation of this conclusion is the identity of absorption and fluorescence spectra of CP(1,5-DAAQ) solutions and copolyamide obtained by tri-staged copolycondensation on the basis of 1,5-DAAQ, i.e. by the method that leads to formation of block-copolymers.

Useful information about the structure of CP(2,6-DAAQ) is contained in the corresponding fluorescence spectra (Figure 4, Tables III, IV). From these it follows that emission bands of the spectra of films and solutions of copolyamides are similar to those of aggregate and molecular forms of 2,6-DBAAQ. It was also found that at 77 K the solutions of 2,6-CPA had bright yellow-green phosphorescence with λ_{max} = 545 nm, also characteristic of 2,6-DBAAQ.[11] From the spectral data cited one can conclude that chromophore fragment inserts randomly into the main chain of the macromolecule. At the same time the bend at 580 nm in the spectral fluorescence curve of CP(2,6-DAAQ) solution (Figure 4) similar to that in emission band of 2,6-DBAAQ aggregate form (Table IV) points to the block structure typical for some chromophore groups.

In the case of CP(4,8-DADOAQ) interpretation of spectral data is much more difficult because neither film nor aggregate form of 4-A-8-DADOAQ and 4,8-DBADOAQ is luminescent (Figure 5, Table IV). As for the solution of this copolyamide, it has fluorescence with λ_{max} = 642 nm. The fluorescence band of this polymer solution is analogous with that of the molecular form of 4-A-8-BADOAQ. At the same time the long-wave absorption band of the film can be fairly well simulated by superposition of absorption bands of aggregate forms of 4-A-8-BADOAQ and 4,8-DBADOAQ (Tables III, IV, Figure 5).

The long-wave absorption band of CP(4,8-DADOAQ) film is also a superposition of absorption bands of the molecular form of 4-A-8-BADOAQ and aggregate form of 4,8-DBADOAQ. The data presented indicate that chromophore fragments in this copolyamide insert into the macromolecule chain as a block localized along the ends of the chain. The structures of the macromolecules studied are shown schematically in Table V. Luminescence of the films and fibers investigated (with the exception of nonfluorescent CP(4,8-DADOAQ)) is presented with fluorescence of the corresponding associated chromophore fragments. Their molecular fluorescence is absent.

Having studied the structure of synthesized copolyamides, let us now consider the motives of formation of one or another structure of copolyamides. From Table V it follows that position and succession of alternation of chromophore links in macromolecules are determined by basicity of traditional (MPDA) and chromophore (DAAQ) diamines, and also by the difference in reactivities of the first and the second amino-groups of corresponding DAAQ. Low reactivity of most DAAQ structures, characterized by the values of ionization constants or acrylation rate constants, leads to formation of block structures in polyamides. The somewhat higher reactivity of 2,6-DAAQ indicates that some chromophore fragments are statistically arranged in the polymer chain.

TABLE V

Relationship between structure of structural-colored polyamides and reactivity of diamines used in synthesis

Type of polyamide	Relative reactivity			Structure of copolymer[c]
	ΔpK_{av}[a]	ΔpK[b]	k_1/k_2	
CP(1,4-DAAQ)	5.34	3.33	38.9	-Φ-Φ-Φ- . . . -AX
CP(4,8-DADOAQ)	5.20	3.21	36.7	-Φ-Φ-Φ- . . . AX . . . -AX
CP(1,5-DAAQ)	5.23	1.34	1.4	-Φ-Φ-Φ- . . . AX . . . AX-Φ-Φ-Φ
CP(2,6-DAAQ)	4.47	1.73	3.9	-Φ-Φ-AX-Φ-AX . . . AX-Φ-AX-Φ-Φ

[a] $\Delta pK_{av} = pK^{MPDA} - pK_{av}^{DAAQ}$ (initial values of the average ionization constants for DAAQ and m-phenylenediamine (MPDA) are taken from Reference 13.

[b] $\Delta pK = pK_1 - pK_2$ (difference between the ionization constant of the first and second DAAQ amino-groups and the ratio of acylation reaction rate constants, K_1/K_2 are taken from Reference 13.

[c] Φ is a link of m-phenyleneisophthalamide; AX is an anthraquinone link.

The data obtained on the structure of aromatic copolymers are in good agreement with those found in literature. In particular, when studying copolyethers synthesized by non-equilibrium copolycondensation, Korshak and co-workers[15] observed analogous dependences between diol reactivity and copolymer structure. The influence of the difference in reactivities of the DAAQ amino-groups contributes to the chain prolongation ability of chromophore oligomers with the end amino-groups. Thus, when inserting diamine with the highest values of ΔpK, as compared with other compounds, into the polyamide chain of 1,4-DAAQ, the chromophore fragment is localized along the ends of macromolecules, as confirmed by the data from Table V.

In conclusion, the present work shows that the molecular mass of structural colored polyamides and the chromophore fragments in their chains are determined by reactivities of the initial diaminoanthraquinones. Introduction of anthroquinone links into the PMPIA chain is shown to only slightly affect the structure and basic physicochemical properties of polyamides but does give a polymer more uniform and homogeneous coloring than that obtained by traditional methods with the same colorants.

Spectral-luminescence properties of solutions and films of polyamides obtained were studied. On the basis of similarity of absorption and fluorescence characteristics of polyamides and the compounds simulating their chromophore links, these polymer structures were determined. Formation of one or another structure was shown to be defined by the differences in reactivity of both comonomers in diamine component and functional groups in chromophore diamine.

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